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Third Quarterly Report

for

CHARACTERIZATION OF NICKEL-CADMIUM ELECTRODES

1 January, 1964 - 1 April, 1964

Contract No. NAS5 - 3477

Prepared by

General Electric Company

Advanced Technology Laboratories
Schenectady, New York

for

Goddard Space Flight Center
Greenbelt, Maryland

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SUMMARY

The objective of this contract is to develop a method of analysis and characterization of the electrodes used in nickel-cadmium sealed cells. It is based primarily on a comparison of detailed polarization measurements of single electrodes before and after periodic operation in selected modes of cyclic testing of cells at three temperature levels 0^{o}, 25^{o}, and $40^{o}C$. A correlation of this data should provide a basis for specifying improved cells for space applications as well as comparing cells from various manufacturers.

During this quarter the bulk of the effort consisted of characterization of electrodes, fabrication of test cells, and putting these cells into the various cycling tests. At the end of the quarter approximately 55% of the electrodes required had been characterized and fabricated into test cells. The shallow depth of discharge and constant voltage, current limited cyclic tests are partially (15%) underway. At the present rate of progress all cyclic tests should be completely underway by the middle of the next quarter.

An apparatus for determining the gassing characteristics of positive electrodes was constructed and preliminary data collected at several charging rates.

The blistering of the positive electrodes observed at the 1C rate occurs during the overcharge portion of the cycle. The plates in the program appear to be more susceptible to the phenomena than another lot of plates obtained from the Battery Products Section. Some of the latter will be inserted into the test program to provide a comparison between the two lots.

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1.0 INTRODUCTION

This report covers the work done during the third quarter of an 18 month program to develop a method for the analysis and characterization of the electrodes used in nickel-cadmium spacecraft batteries.

The goal of the program is to develop a correlation between detailed characterization data obtained on single electrodes and the behavior of these electrodes in cells in various modes of cyclic operation. Such a correlation will provide a basis for specifying improved cells for space application and comparing cells from various manufacturers.

A breakdown of the program into tasks is given in Table I. The test program is divided into two parts: one, the initial characterization testing of plates (Task IV); and the other, the cycling of cells made from characterized plates in selected modes of operation (Tasks V - VII). Periodically test cells will be removed from tests and the individual electrodes will be recharacterized and examined for changes in physical properties and comparisons made to the original characterization data.

The initial characterization will be made by analysis of data taken in single electrode experiments based on the use of continuous recording of charge-discharge curves under various testing regimes. The characterization information will include: 1) polarization of each electrode under various conditions, 2) complete charge and discharge curves showing electrode capacity, impurity levels, onset of gassing, graphitic and antipolar capacity, and reproducibility of cell operation, and 3) the onset of changes in capacity under various operating conditions.

All plates in the program will be SAFT type VO, prepared as for space cells. Tests will be made at three temperatures: 0^{o}, 25^{o}, and $40^{o}C$. Failure analysis on cycled cells will be made, using visual, mechanical, chemical and electrochemical procedures.

During this quarter work continued on the characterization of electrodes, the fabrication of test cells, and the insertion of these cells into the various cyclic tests. Fifty-five percent of the electrodes required have been characterized and fabricated into test cells. Test cells are cycling in two of the three types of cyclic tests to be performed and the balance is expected to be underway by the middle of the next quarter.

The blistering of the positive electrode at the 1C rate occurs during the overcharge portion of the charge cycle. The lot of plates being used in the program appears more susceptible to blistering than another lot obtained from the Battery Products Section. Some plates from the latter will be inserted into the test program to provide a comparison between the two.

TABLE I
PROGRAM TASKS
NAS5 - 3477

	TASK		MEASUREMENTS
I	Control and Recording Equipment Design and fabrication of test equipment.		None.
II	Test Cell Assemblies Design and fabrication of test cells.		None.
III	Electrode Preparation Electrochemical cleaning of reference and cell electrodes, inspection and welding of identification tabs.		Capacity check and weight.
IV	Characterization Tests - CA and CB C-A Constant current charging at C/10, C/5 and C C-B Constant current discharging at C/10, C/5 and C	C-A	Determine charge curve. Determine rate of gassing from electrodes. Determine rate of O_2 recombination.
		C-B	Determine discharge curve.
V	Shallow Discharge Cycling Tests C-C Constant current cycling to 25-35% range to determine memory effects	C-C	Make periodic capacity determination. Make analysis of physical properties. Recovery test.
VI	Random Discharge Tests R-A Random discharges averaging 10%, 25%, 50% and 75% depth of discharge over a 6-day period using Gaussian and rectangular distribution for discharge periods.	R-A	Periodic charge and discharge curve. Recharacterization tests.
VII	Constant Voltage, Current Limited Charging Cycling Tests R-B Charge at C/5 rate and discharge at C/2 rate to 0.9 volts.	R-B	Periodic charge and discharge curve. Recharacterization tests.

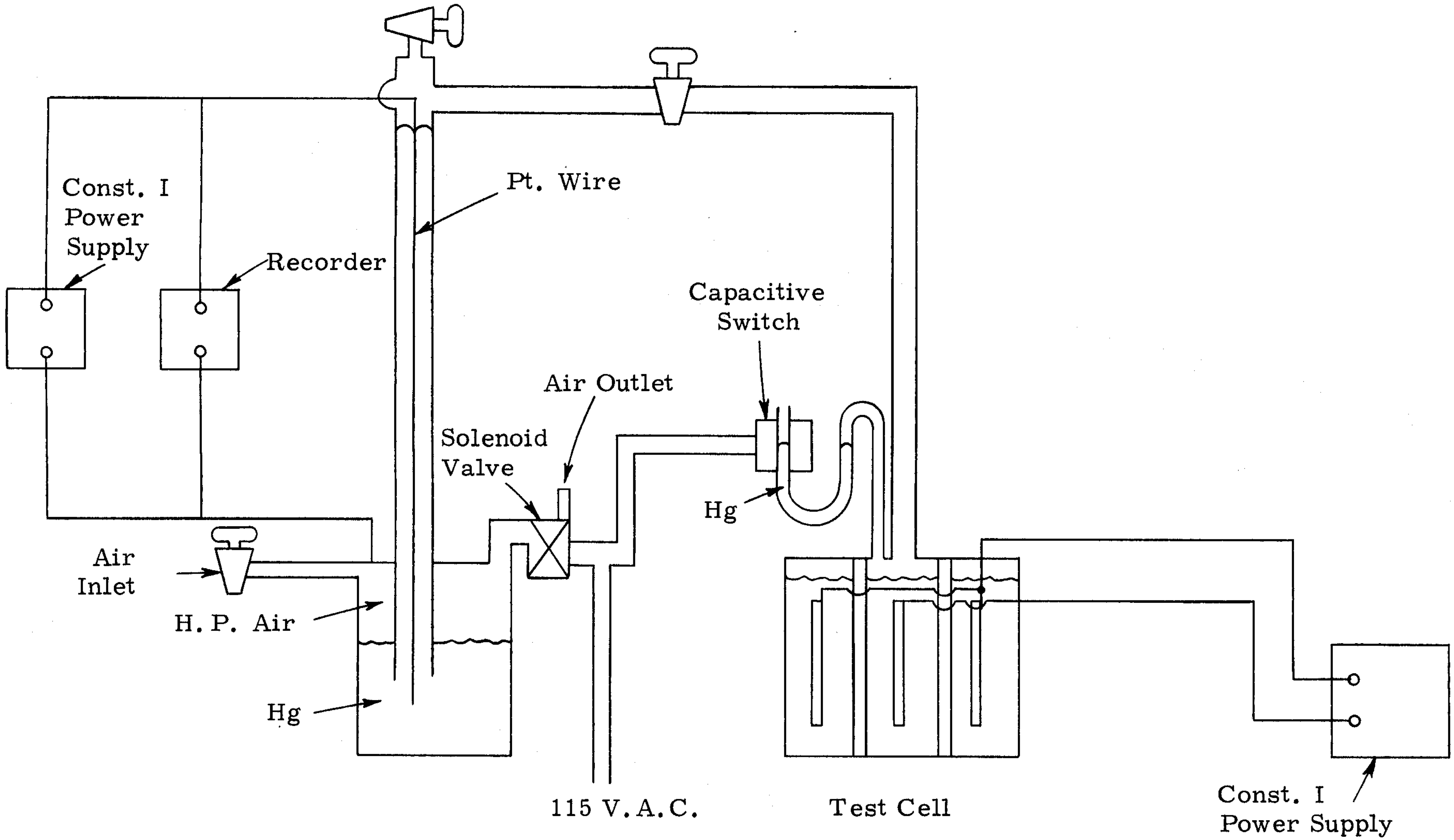

Figure 1

GAS EVOLUTION MEASURING APPARATUS

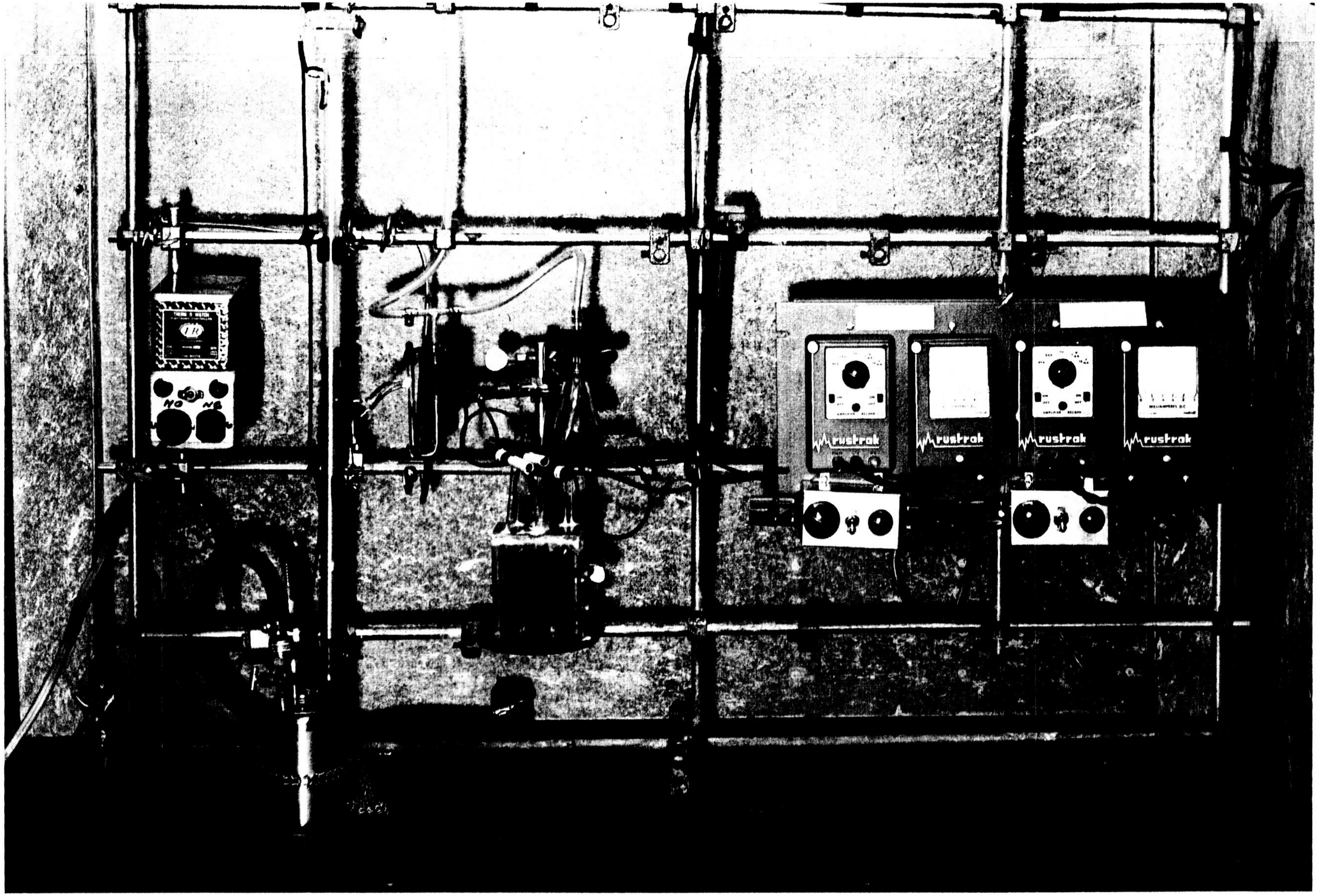

Figure 2. Gas Evolution Measuring Apparatus

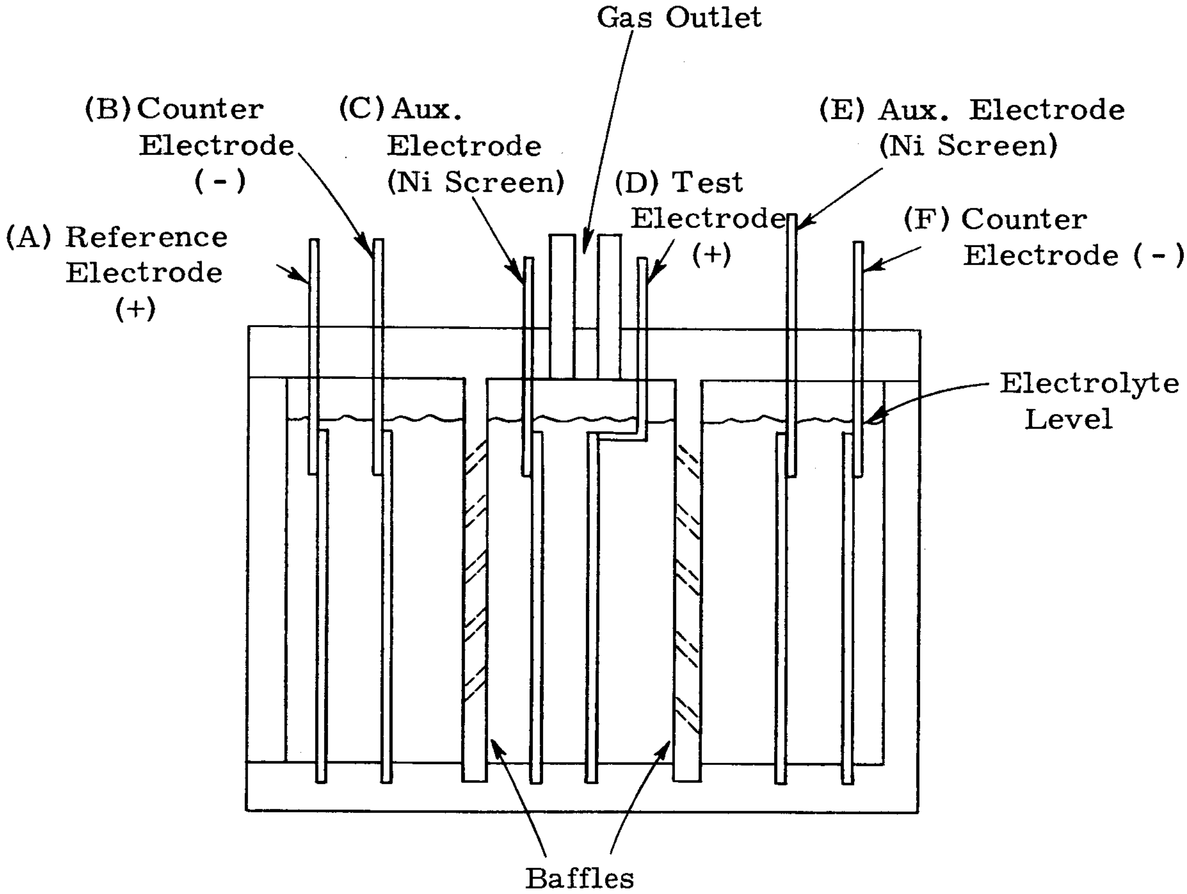

Figure 3

GAS EVOLUTION TEST CELL

2.0 DISCUSSION

The work accomplished during this quarter included the continuation of the initial characterization of electrodes, the initiation of gas rate studies on nickel electrodes, the assembly of cyclic test cells and putting these cells on cyclic tests (Tasks V - VII) as outlined in Table I. In addition supporting studies were conducted to determine the conditions under which blistering and pimpling of the nickel electrodes, reported in the last quarterly report occurred. The details of the work accomplished are reported in the following sections.

2.1 Test Cell Assemblies - Task II

A test cell assembly and apparatus was constructed to measure the rate of evolution of gases from positive electrodes as a function of charging rate. These tests are part of the initial characterization tests of Task IV.

A schematic diagram of the experimental set up is shown in Figure 1 and a photograph of the equipment is shown in Figure 2. The volume of gas is determined by measuring and recording the voltage drop across the platinum wire in the gas burette as the mercury column drops with gas accumulation.

A constant current is passed through the wire by means of power supply, as gas accumulates in the burette, the mercury column is automatically lowered by means of a solenoid valve which vents the high pressure air from the mercury reservoir. The solenoid valve is actuated by a mercury capacitive switch. The pressure differential required to operate the switch is 3 mm. Hg.

The details of the gas evolution test cell assembly are shown in Figure 3. In operation to measure the gassing of an uncharged positive electrode (D) a current is passed between the positive electrode (D) and uncharged cadmium counter electrodes (B) and (F). The capacity of the two counter electrodes is sufficient to prevent hydrogen evolution well beyond the point where the nickel electrode is fully charged. The additional screen electrodes in the test cell provide for the complete discharge of the counter electrodes and test electrode after each gas rate measurement. The equipment is limited to accumulating a gas volume of 100 cc. An improved apparatus is being constructed to permit longer runs.

The cell design minimizes the recombination of oxygen at the counter electrodes and at charging rates of C/10 or greater does not introduce significant errors into the measurements.

Preliminary gas measurements on nickel electrodes have been made and are reported in the next section.

TABLE II

Parameters for Depth of Discharge Distribution Curves

Average Depth Discharge	Standard Deviations					
$\bar{x}$	σ^{*}	σ^{**}	p	q	m	n
.10	.0250	.0253	126	14	252	28
.25	.0625	.0619	36	12	72	24
.50	.1250	.1213	8	8	16	16
.75	.1875	.1936	1	3	2	6

*nominal value of σ

**actual value of σ

2.2 CA-CB Test - Task IV

A total of 340 plates have been characterized (170 positives and 170 negatives). The majority of these have been characterized at a nominal C/10 rate at room temperature. The cycle conditions for the C/10 rate tests were, charge for 720 minutes at 0.140 amp. and discharge for 600 minutes at 0.160 amps.

The correlation of the variation in capacity over the seven characterization cycles is in progress. The data for 60 plates have been tabulated from the original potential-time recorder traces.

2.2.1 Oxygen Evolution - As part of the initial characterization data, the start of oxygen evolution and the rate of oxygen evolution as a function of charging rate will be determined for a limited number of positive electrodes. The data will provide a reference point for comparison with similar measurements which will be made on plates periodically removed from the cyclic tests.

These experiments were started during the later part of this quarter using the equipment and procedure outlined in section 2.1. Preliminary results obtained on a single nickel electrode which had not been electrochemically cleaned are shown in Figures 4, and 5. The first chart, Figure 4, shows the rate of gas evolution as a function of the state of charge of the electrode with charging rate as a parameter. The state of charge is expressed as the ratio of charge returned to the test cell, corrected for the amount of charge that has gone into gassing during the charging period, divided by the capacity of the electrode. The capacity in each case is the ampere-hour value delivered at a C/2 discharge rate to the knee point of the nickel electrode potential-time curve. This corresponds approximately to a voltage cutoff of 0.9 volts for a nickel-cadmium cell.

The second chart, Figure 5, shows the fraction of the charge current being converted to oxygen as a function of the state of charge term corrected for charge that went into oxygen evolution.

The curve for the 200 ma charge rate shows a poorer charge acceptance than the other curves. This attributed to the fact that this was the first run on the electrode which was in the unformed condition.

During the next quarter measurements on additional electrodes will be made to determine reproducibility of results from electrode to electrode. Measurements will be made at three charging rates corresponding to C/10, C/5, and C at room temperature. A few measurements will also be made on electrodes which developed blisters during characterization at the 1C rate to determine if blistering has any detrimental affect on the gassing behavior of the electrode.

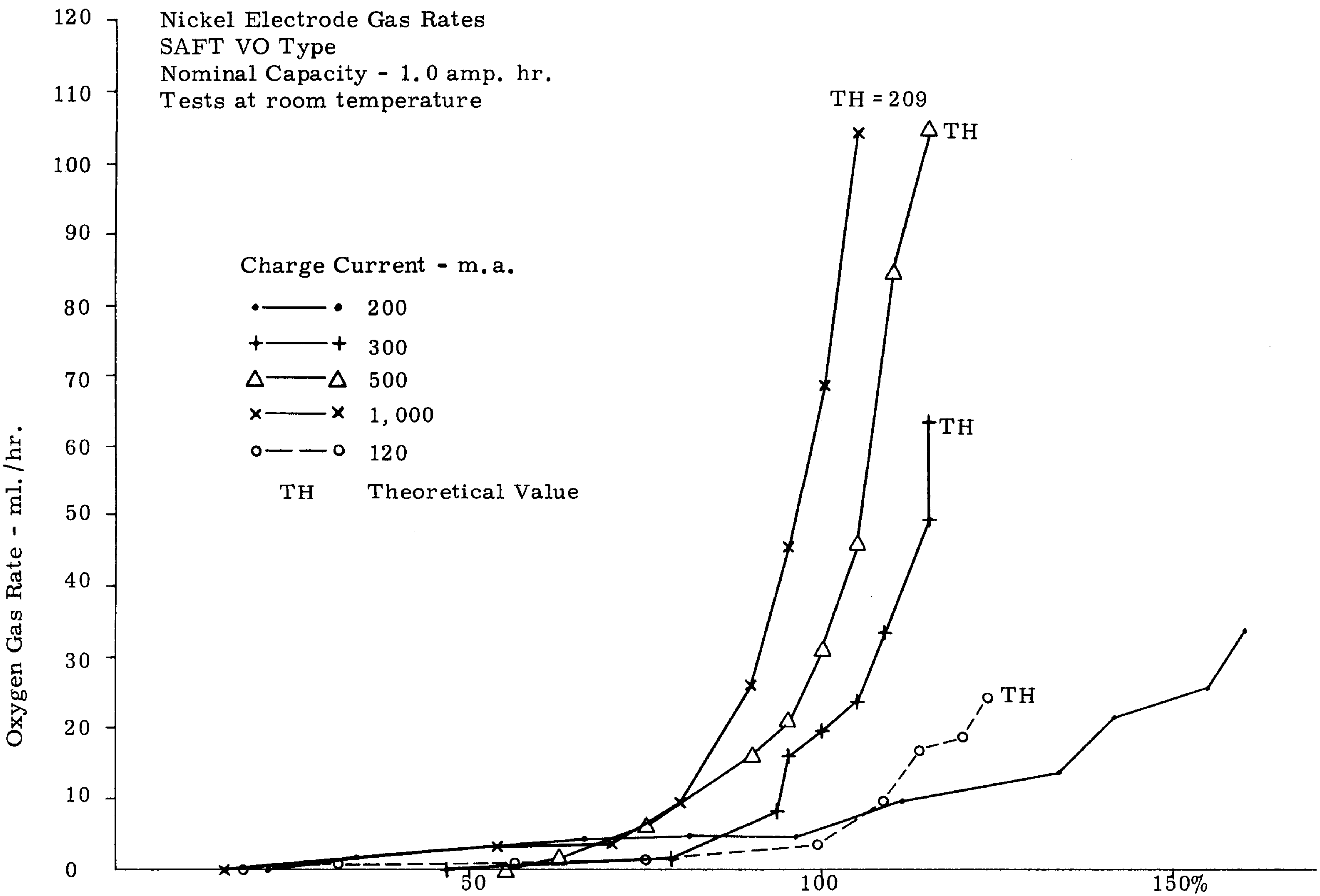

Figure 4
State of Charge $\frac{\text{(Total Input - Gas Equivalent) amp. hr.}}{\text{Discharge Capacity - amp. hr.}}$

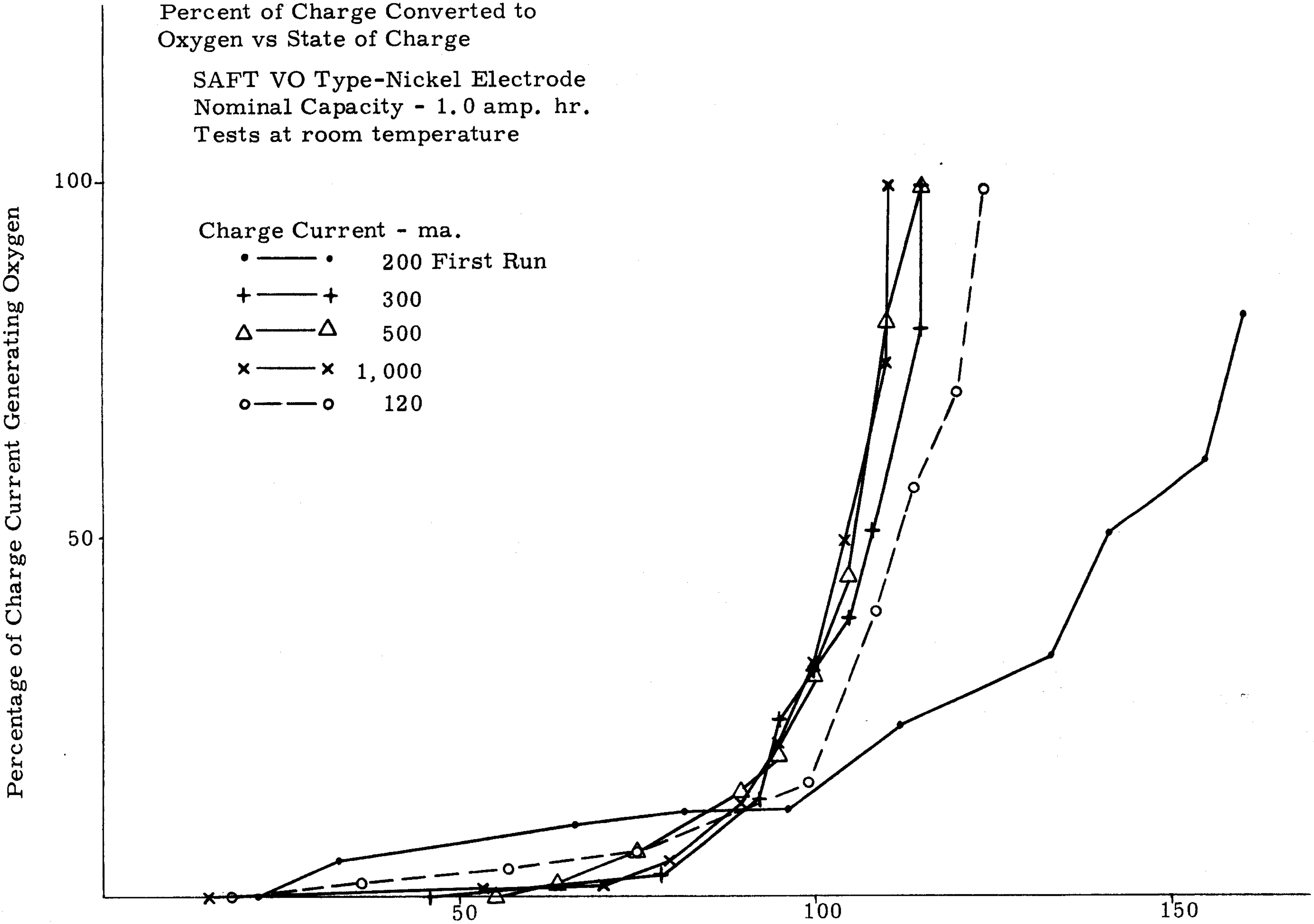

Figure 5

State of Charge - (Total Input - Gas Equivalent) - amp. hr. / Discharge Capacity - amp. hr.

2.3 C-C Tests - Task V

The balance of the cells of these tests were fabricated and three out of the nine cells were started on the 25% depth of discharge cyclic testing. The cycle conditions are discharge for 35 minutes at 1.7 amperes and charge for 55 minutes at 1.3 amperes.

The disassembly of cells and examination for memory effect is planned to start during the next quarter.

2.4 R-A Tests - Task VI

These tests are designed to determine the effect of cell operation in which the average depth of discharge for all cycles over a period of a week is fixed at pre-determined levels of 10, 25, 50 and 75%. At each level, the depth of discharge for a given cycle is selected on a random basis. Two types of distribution for the depth of discharge of individual cycles over the period of a week are to be used: one based on a Beta distribution and the other a rectangular distribution.

The generation of the distributions for these functions was done by the statistical group in the laboratory. The Beta distribution is defined by

$$f(x) = \frac{\Gamma(p+q)}{\Gamma(p)\,\Gamma(q)} (1-x)^{p-1} \; x^{q-1} \qquad 0 \leq x \leq 1$$

whose shape is determined by the parameters p and q. The parameters can be uniquely specified from a knowledge of the desired mean and standard deviation (a measure of dispersion about the mean) as follows:

$$\bar{x} = \frac{q}{p+q}$$

$$\sigma^2 = \frac{pq}{(p+q+1)\,(p+q)^2}$$

where $\bar{x}$ is the mean depth of discharge we wish to simulate and σ^2 is the square of the standard deviation which measures the variability of the individual depth of discharge about the mean.

The mean depth of discharges are assumed; hence only the standard deviations need be determined. It was reasoned that the spread about the mean would be directly proportional to the mean, i.e., the higher the depth of discharge, the higher the dispersion about the mean depth of discharge. It was further assumed that this relationship, expressed in terms of the coefficient of variation $\sigma/\bar{x}$, would be a constant, c. The value of c = 1/4 was chosen. Table II shows the mean, variance, p and q of the four depth of discharges. Due to the method of generating the Beta variables, 2p and 2q were required to be integers. This caused a small deviation from the desired values of σ and is shown in Table II.

<u>Generation of the Beta Random Variables</u>

There is no simple, direct method for generating random variables from a Beta distribution since the integral,

$$\int_{o}^{a} (1-x)^{p-1} \quad x^{q-1} \; dx \qquad 0 < a < 1$$

cannot be evaluated by elementary methods. However, it is known from statistical theory that the variable

$$z = \frac{\sum_{i=1}^{n} w_i^2}{\sum_{i=1}^{n} w_i^2 + \sum_{i=1+1}^{n+m} w_i^2}$$

where w_i (i = 1, 2, ..., m+n) are independent variables each generated from a normal distribution with mean zero and variance one, has a Beta distribution with parameters $p = \frac{m}{2}$ and $q = \frac{n}{2}$. (See Appendix I for derivation). The w_i can be obtained from standard random normal deviate tables or, as in this case, generated on a digital computer.

The generated sets of z's (200 for $\mu = .10$, 100 for $\mu = .25$, 50 for $\mu = .50$, and 25 for $\mu = .75$) can be used to simulate random depth of discharges based on the Beta distribution model.

The random discharge distributions which will be used in the tests are plotted in Figures 6 and 7. These distributions have been put on the tape which controls the sequence of charge and discharge of RA cyclic controller equipment.

The cycle conditions for these tests are to charge at 100 ma (C/10 rate) to 120% of previous discharge and discharge at 200 ma (C/5 rate).

The start of these tests was delayed by the burnout of six latching relay coils in the control equipment. Replacement coils have been ordered and it is expected that the equipment will be ready for use in the third quarter.

TABLE III

EFFECT OF EXCESS CHARGE CONDITIONS ON PHYSICAL CHARACTERISTICS OF NICKEL ELECTRODES AT ROOM TEMPERATURE IN 25% AND 31% KOH ELECTROLYTE

GE

KO-15- 1.4 amp. hr. Nominal Capacity

25% KOH - One Plate
C/10-C/7-C/1.4 ---535-675-500% Excess

No Effect

31% KOH ---One Plate

C/10-C/7-C/1.4 ---535---675-500% Excess

No Effect

SAFT

VO- 1.0 amp. hr. Nominal Capacity

25% KOH --- Three Plates
C/7-C/5-C/1 ---960-950-700% Excess

No Effect

C/7-C/1 ------340-700% Excess

No Effect

C/5 ----------410% Excess

Blisters

31% KOH --- Two Plates

C/7 ----------260% Excess

Pimples

C/7 ----------110% Excess

Pimples

Random Discharge Distributions

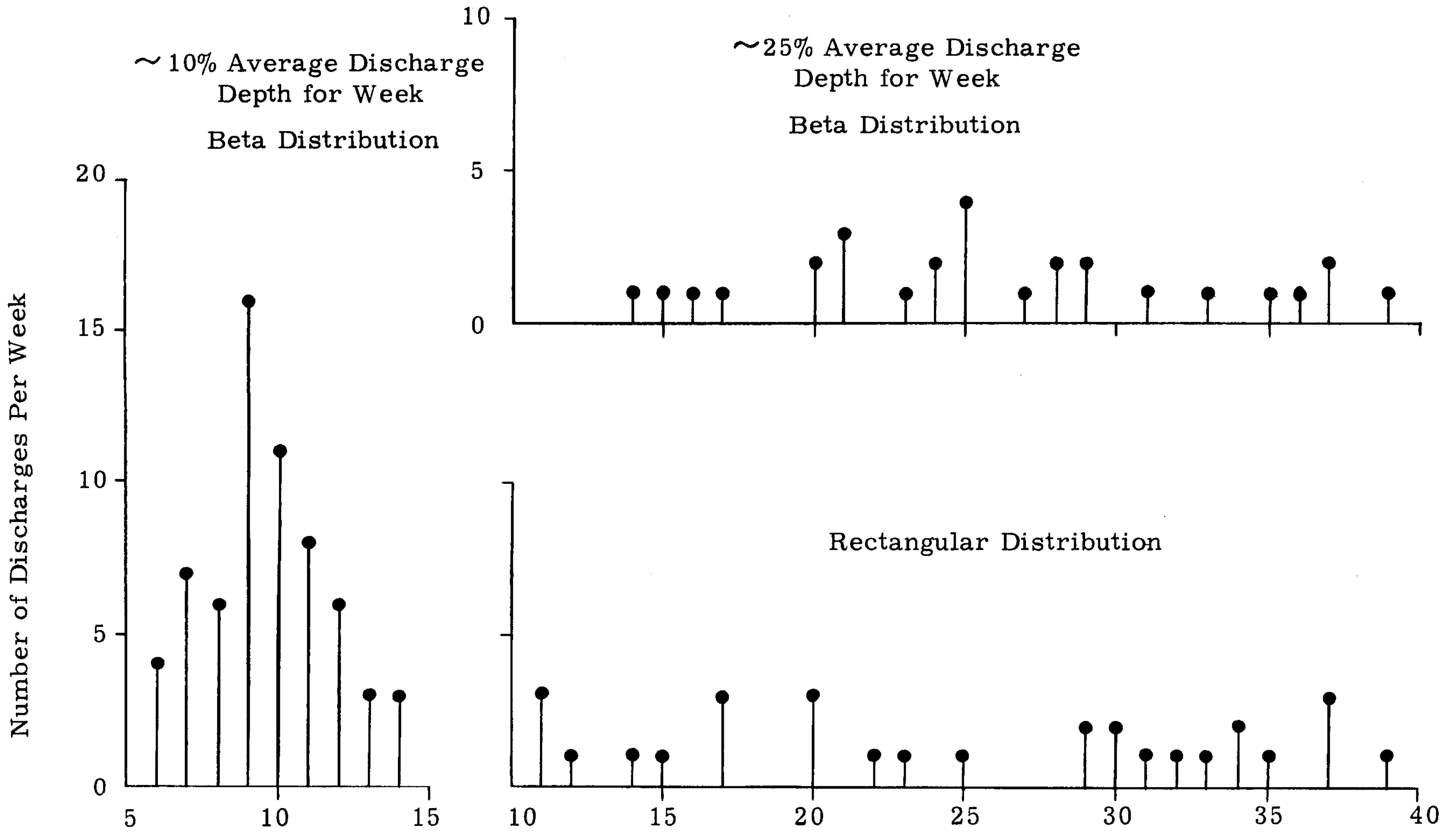

Figure 6

Percent Depth of Discharge - Individual Cycle

Random Discharge Distributions

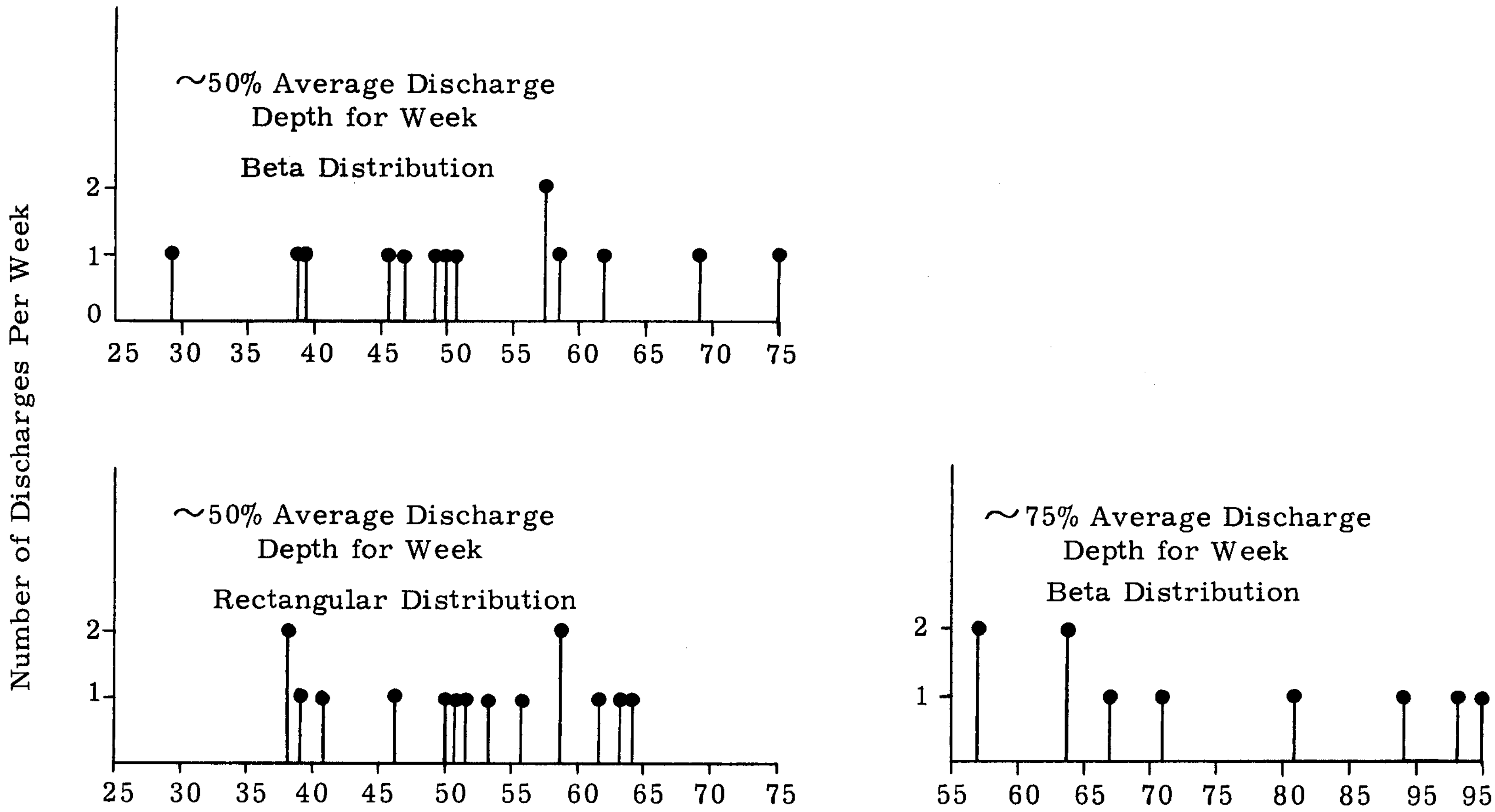

Figure 7

Percent Depth of Discharge - Individual Cycle

2.5 R-B Tests - Task VII

Two out of six cells for this series of tests were fabricated and put on cyclic test during the quarter. These tests are designed to determine the effect of cyclic operation under constant voltage, current limited charging conditions. Charge voltages are 1.50, 1.47, and 1.42 v respectively at 0^{o}, 25^{o} and 40^{o} centigrade with the current limited at 0.80A for 7 3/4 hours. This is followed by discharge at 2.0A to 0.9 volts followed by a rest period for a total of 10 3/4 hours per cycle.

2.6 Positive Electrode Blistering Problem

As discussed in the second quarterly report nickel electrodes were observed to develop blisters and pimples when characterized at the 1C rate in the CA-CB tests. Supporting studies were carried out during this quarter to determine during what portion of the cycle the blistering occurred, under what conditions, and whether the particular lot of plates being used in the program was more susceptible than other lots.

In the first part of these studies additional plates from the same lot being used in the program were characterized at the 1C rate and the results confirmed that the phenomena was reproducible. Similar results were obtained on tests of another batch of plates from the same original shipment from SAFT.

Additional plates removed from commercial vented type cells which have the same size and type plates being used in the program also showed blistering when characterized at the 1C rate.

Pretreatments such as forming the plates at low charge and discharge rates (C/20 to C/10) prior to testing at 1C rates showed some reduction in the severity of the blistering both with respect to number and size of blisters per plate.

At this point a controlled experiment was set up with new plates made in Gainesville but of the same type construction, VO, and SAFT made plates being used in the program. The new plates (KO-15) have a nominal capacity of 1.4 amp-hr. versus 1.0 amp-hr. for plates being used in the program. Test cells consisting of two nickel electrodes immersed in 25% and 31% KOH were made. The cells were connected in series and charged at various rates so that one plate in a cell was being continuously charged and the other discharged. Plates were periodically examined after various amounts of excess charging had occurred.

The significant results from those tests are summarized in Table 2.

The results observed were that none of the electrodes on overdischarge showed evidence of pimples. Electrodes on overcharging showed pimples and minor amounts of blisters compared to results from the 1C characterization tests. The plates being used in the program seem to be more prone to blistering than the KO-15 plates based on all the tests made to date. The other significant parameter is that the higher concentration of potassium hydroxide promotes the phenomena at lower percentages of overcharge.

The conclusion is drawn that plates being used in the program are more susceptible to pimpling than the KO-15 plates. The severe blistering at the 1C rate in characterization tests starts with pimples formed during the portion of the cycle overcharge and higher charge rates and are enlarged to blisters during hydrogen evolution in the discharge portion of the cycle.

On the basis of these results it is planned to insert positive KO-15 plates cut down to the same size as plates now in use into the testing program. Differences in behavior of the electrodes in cyclic testing as well as characterization results can be determined. The results may also indicate the relative significance of blistering with respect to behavior in the cyclic tests.

3.0 PROGRAM FOR NEXT QUARTER

The characterization test CA-CB for the SAFT - VO type electrodes will be completed and all cyclic tests with these electrodes will be underway.

The measurements on the evolution of oxygen from positive electrodes will continue, using good characterized SAFT-VO positives, KO-15 positives and some blistered positives.

Some of the shallow cycling test cells will be removed from test, checked for capacity, examined and recharacterized.

4.0 NEW TECHNOLOGY REPORT

There were no new developments during this quarter which come under the "New Technology" clause of this contract.

APPENDIX I

Generation of Beta Variables

The Beta distribution defined by

$$\frac{\Gamma(p+q)}{\Gamma(p)\,\Gamma(q)}\,(1-x)^{p-1}\quad x^{q-1}\qquad 0\leq x\leq 1$$

is a limited range distribution whose shape is determined by its two parameters p and q and whose mean and variance are given by

$$\frac{q}{p+q}\ \text{and}\ \frac{pq}{(p+q+1)(p+q)^2}\quad .$$

Since integrals of the form

$$\int_o^a (1-x)^{p-1}\quad x^{q-1}\ dx \qquad o < a < 1$$

cannot be directly evaluated it is not possible to simply generate random variables from the Beta distribution. Neither do there exist tables of random variates from this family of distributions.

However it is possible, using normally distributed variables to generate Beta variables as follows.

Let w_i be a random variate from a normal distribution with mean zero and variance one for i = 1, 2, ..., m+n such that the w_i's are independent.

Then $v_n = \sum_{i=1}^{n} w_i^2$ is distributed as a chi-square variable with parameter n, i.e.,

$$f(v_n) = \frac{1}{2^{n/2}}\,\frac{1}{\Gamma(\frac{n}{2})}\,v_n^{\,n/2-1}\,e^{-\frac{1}{2}v_n}\quad .\quad 0\leq v_n\leq\infty$$

We now obtain the distribution of

$$y = \frac{v_m}{v_n}$$

where v_n and v_m are independent chi-square variables with parameters n and m.

$$f(v_n, v_m) = \frac{1}{2^{\frac{n+m}{2}}} \frac{1}{\Gamma(\frac{n}{2})\Gamma(\frac{m}{2})} v_n^{\frac{n}{2}-1} v_m^{\frac{m}{2}-1} e^{-\frac{1}{2}(v_n+v_m)}$$

Changing variables we

let $y = \frac{v_m}{v_n}$

$v_n = v_n$

The Jacobian of the transformation,

$$J = v_n$$

$$f(y, v_n) = \frac{1}{2^{\frac{n+m}{2}}} \frac{1}{\Gamma(\frac{n}{2})\Gamma(\frac{m}{2})} v_n (y\, v_n)^{\frac{m}{2}-1} v_n^{\frac{n}{2}-1} e^{-\frac{1}{2}(y\, v_n + v_n)}$$

$$= \frac{1}{2^{\frac{n+m}{2}} \Gamma(\frac{n}{2}) \Gamma(\frac{m}{2})} y^{\frac{m}{2}-1} v_n^{\frac{n}{2}+\frac{m}{2}-1} e^{-\frac{1}{2} v_n(y+1)}$$

$$f(y) = \frac{1}{2^{\frac{n+m}{2}} \Gamma(\frac{n}{2}) \Gamma(\frac{m}{2})} y^{\frac{m}{2}-1} \int_0^\infty v_n^{\frac{n}{2}+\frac{m}{2}-1} e^{-\frac{1}{2} v_n(y+1)} dv_n$$

$$= \frac{1}{2^{\frac{n+m}{2}} \Gamma(\frac{n}{2}) \Gamma(\frac{m}{2})} y^{\frac{m}{2}-1} \frac{\Gamma(\frac{n}{2}+\frac{m}{2})}{\left[\frac{1}{2}(y+1)\right]^{(\frac{n}{2}+\frac{m}{2})}}$$

$$= \frac{\Gamma(\frac{n+m}{2})}{\Gamma(\frac{n}{2}) \Gamma(\frac{m}{2})} y^{\frac{m}{2}-1} (y+1)^{-(\frac{n+m}{2})}$$

Changing variables again

we let $$z = \frac{\sum_{i=1}^{n} w_i^2}{\sum_{i=1}^{n} w_i^2 + \sum_{i=n+1}^{n+m} w_i^2} = \frac{v_n}{v_n + v_m} = \frac{1}{1 + \frac{v_m}{v_n}}$$

or $z = \frac{1}{1+y}$ $\therefore$ $y = \frac{1-z}{z}$

The Jacobian of the transformation is $-\frac{1}{z^2}$

$$f(z) = \frac{\Gamma\left(\frac{n+m}{2}\right)}{\Gamma\left(\frac{n}{2}\right)\Gamma\left(\frac{m}{2}\right)} \left(\frac{1-z}{z}\right)^{\frac{m}{2}-1} z^{\frac{n+m}{2}} \frac{1}{z^2}$$

$$f(z) = \frac{\Gamma\left(\frac{n+m}{2}\right)}{\Gamma\left(\frac{n}{2}\right)\Gamma\left(\frac{m}{2}\right)} (1-z)^{\frac{m}{2}-1} z^{\frac{n}{2}-1}$$

which is a Beta distribution with $p = \frac{m}{2}$ and $q = \frac{n}{2}$.

Thus if we take m and n independent variables from a normal distribution with mean zero and variance one and form the statistic

$$z = \frac{\sum_{i=1}^{n} w_i^2}{\sum_{i=1}^{n} w_i^2 + \sum_{i=n+1}^{n+m} w_i^2}$$

the z's so generated will follow a Beta distribution with $p = \frac{m}{2}$ and $q = \frac{n}{2}$.